Supporting Information

Highly Selective Luminescent Sensing of Fluoride and Organic Small-Molecule Pollutants Based on Novel Lanthanide Metal-Organic Frameworks

Jing-Min Zhou, Wei Shi[*]*, Na Xu and Peng Cheng*[*]

Department of Chemistry, Key Laboratory of Advanced Energy Material Chemistry (MOE), Nankai University, Tianjin 300071, People's Republic of China

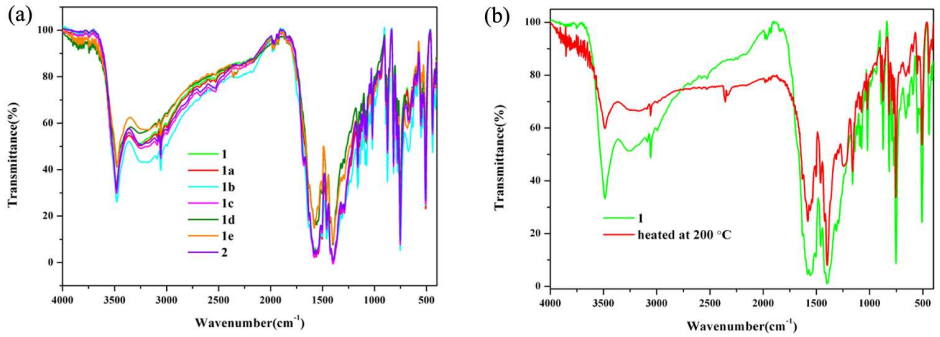

Figure S1 The FTIR Spectra of (a) **1**, **1a-e**, and **2**, and (b) heated sample.

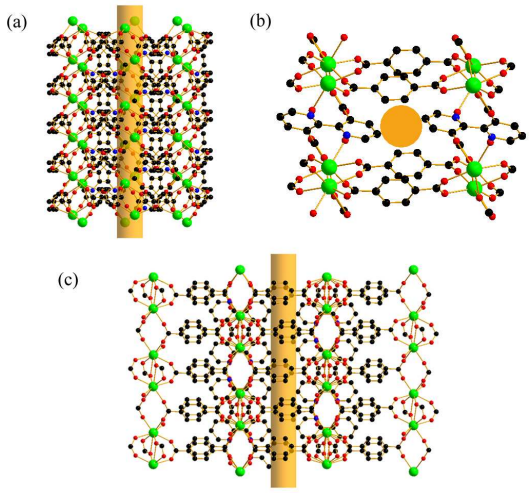

Figure S2 The 1D channel in the framework viewed along the direction (a) [1, 0, 0], (b) [0, 1, 0], and (c) [0, 0, 1].

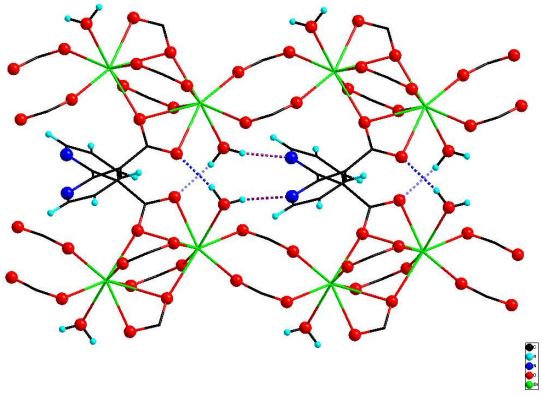

Figure S3 The schematic diagram of hydrogen bonds in Ln-MOF **1**. (Blue: O---H, violet: N---H)

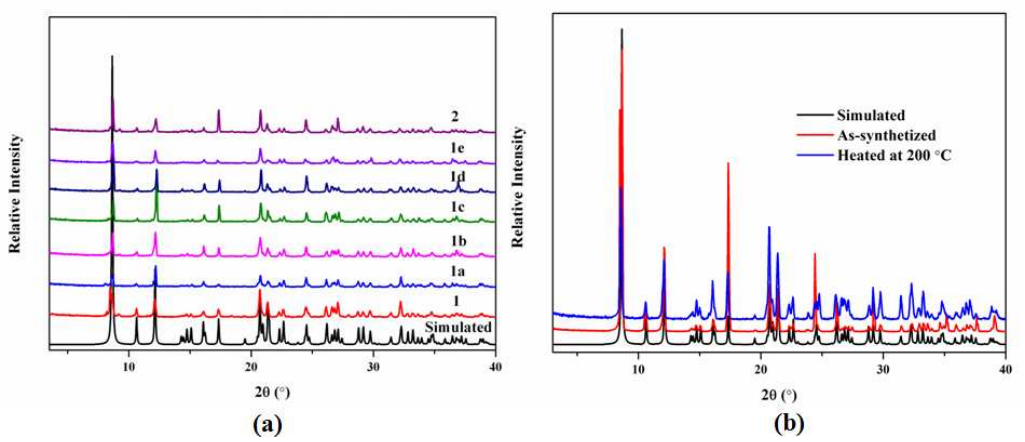

Figure S4 Simulated and experimental PXRD patterns of Ln-MOFs (a) **1**, **1a-e** and **2**, and (b) heated sample of **1**.

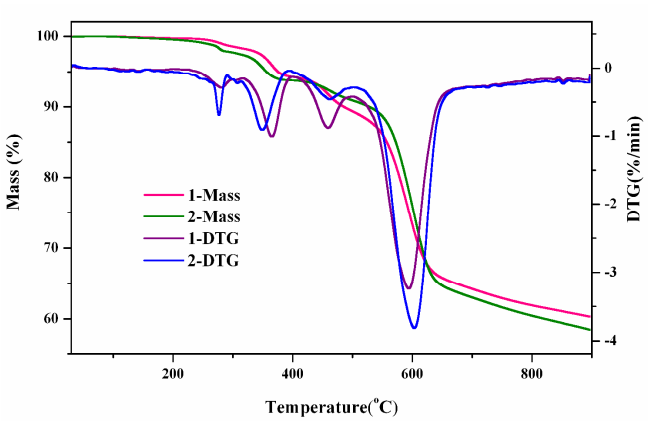

Figure S5 TGA curves of Ln-MOFs **1** and **2**.

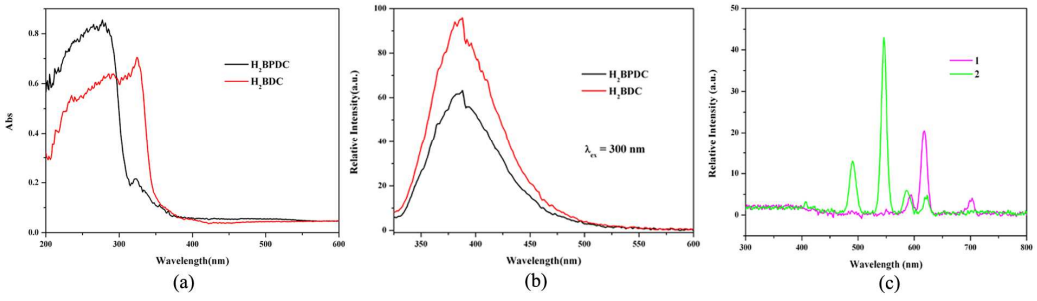

Figure S6 Absorption **(a)** and emission **(b)** spectra of ligands H_2BPDC and H_2BDC, and **(c)** PL spectra of Ln-MOFs **1** and **2**.

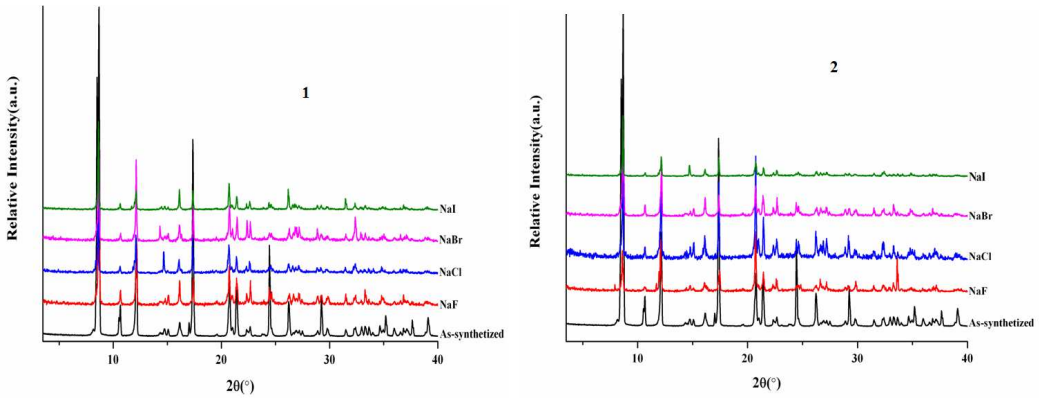

Figure S7 PXRD patterns of Ln-MOFs **1** and **2** after immersing in NaX (X = F^-, Cl^-, Br^-, I^-) solutions (10^{-2} M) for 48 hours.

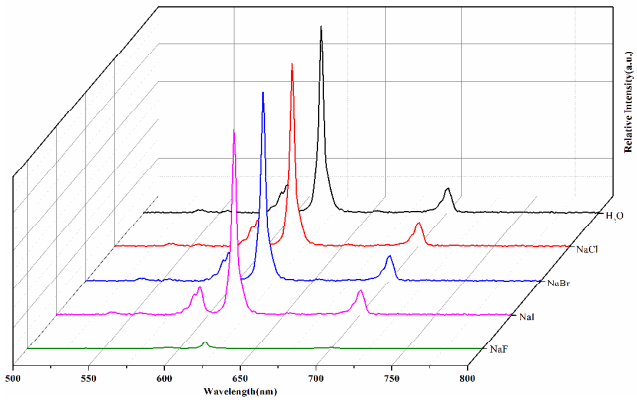

Figure S8 The PL spectra of Ln-MOF **1** dispersed into H_2O and NaX (X = F^-, Cl^-, Br^-, I^-) solutions (10^{-2} M) (excited at 300 nm).

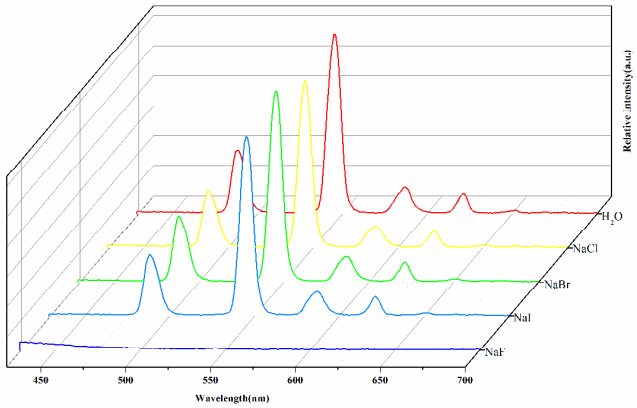

Figure S9 The PL spectra of Ln-MOF **2** dispersed into H_2O and NaX (X = F^-, Cl^-, Br^-, I^-) solutions (10^{-2} M) (excited at 300 nm).

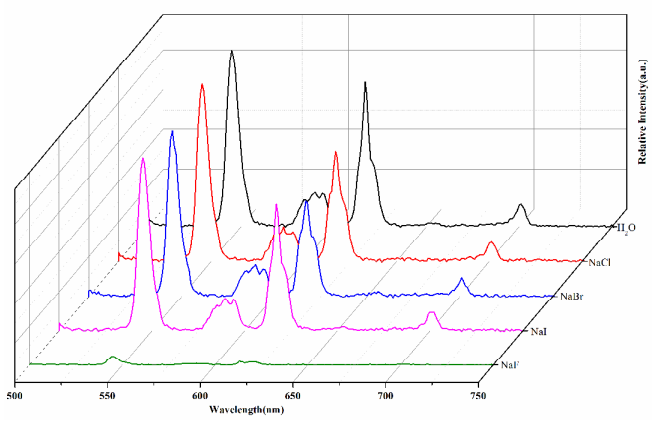

Figure S10 The PL spectra of doped Ln-MOF **1a** dispersed into H_2O and NaX (X = F^-, Cl^-, Br^-, I^-) solutions (10^{-2} M) (excited at 300 nm).

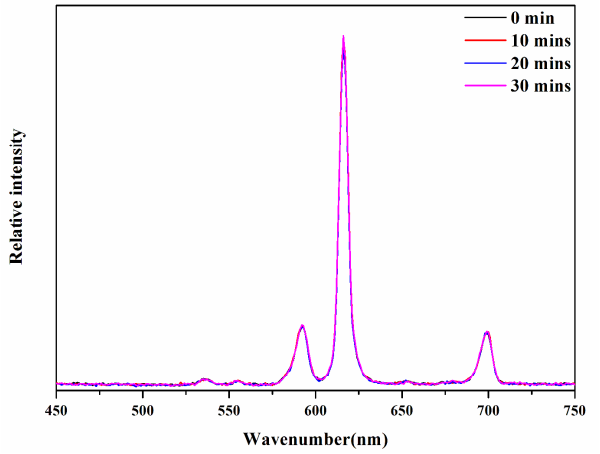

Figure S11 The PL spectra of Ln-MOF **1** without NaF in H_2O every ten minutes.

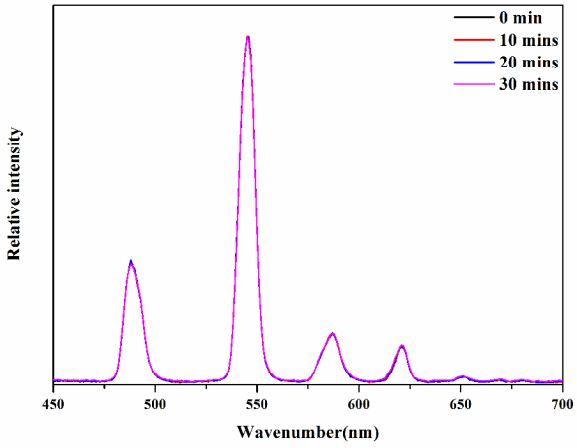

Figure S12 The PL spectra of Ln-MOF **2** without NaF in H_2O every ten minutes.

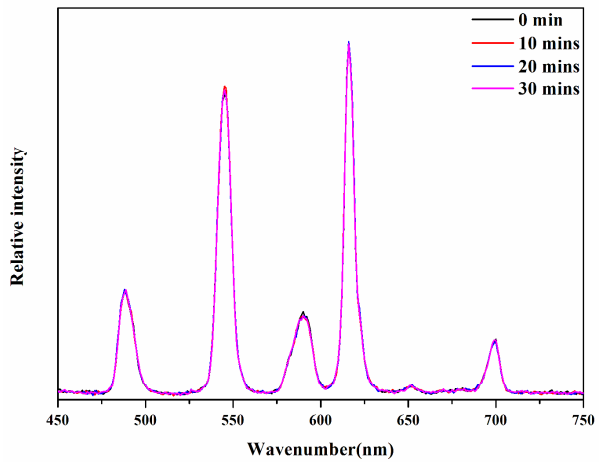

Figure S13 The PL spectra of doped Ln-MOF **1a** without NaF in H_2O every ten minutes.

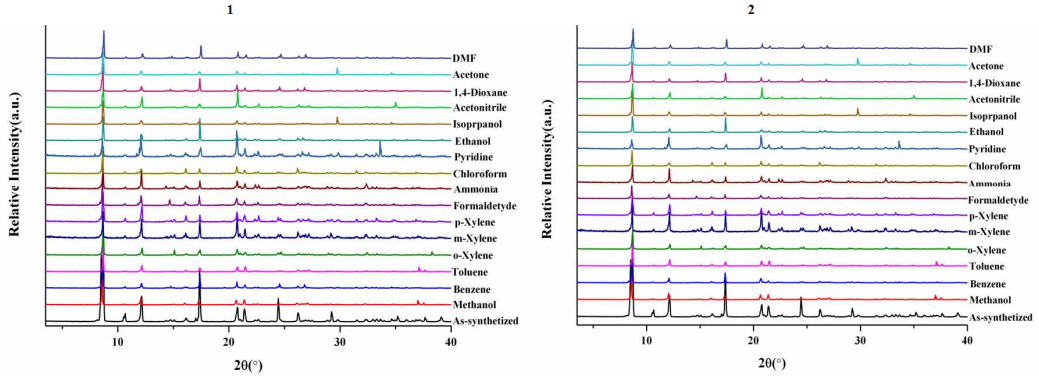

Figure S14 PXRD patterns of Ln-MOFs **1** and **2** after immersing in different solvents for 48 hours.

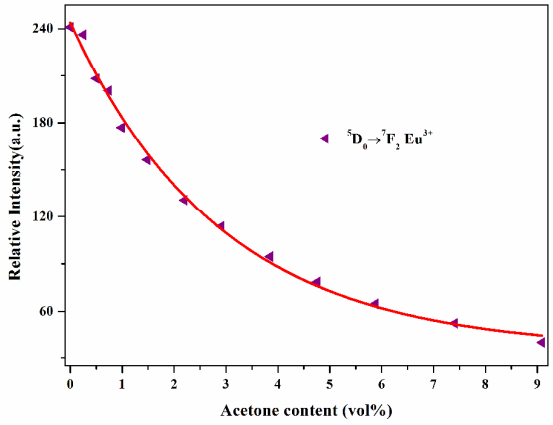

Figure S15 The $^5D_0 \rightarrow {}^7F_2$ transition intensity of Eu^{3+} for 1,4-dioxane suspension of Ln-MOF **1** as a function of acetone content.

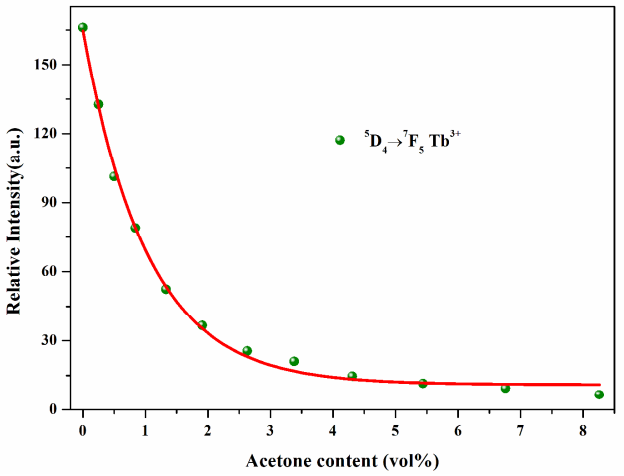

Figure S16 The $^5D_4 \rightarrow {}^7F_5$ transition intensity of Tb^{3+} for toluene suspension of Ln-MOF **2** as a function of acetone content.

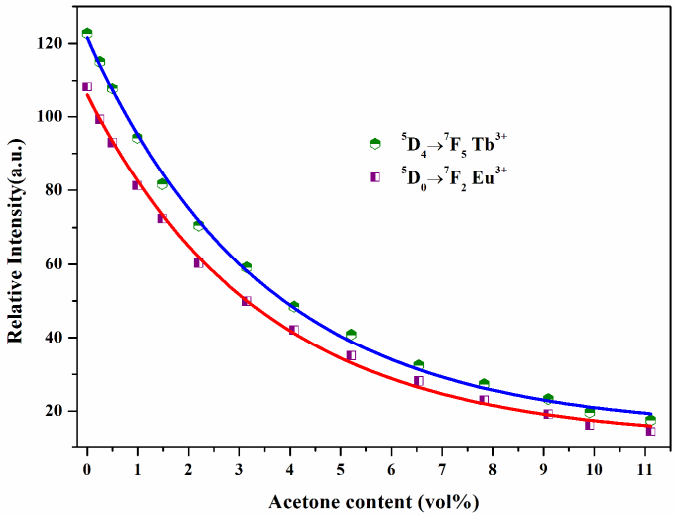

Figure S17 The $^5D_0 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_5$ transition intensities of Eu^{3+} and Tb^{3+} for formaldehyde suspension of **1a** as a function of acetone content.

Table S1 The chemical composition of the doped samples **1a-e** by ICP.

Compounds	The mole ratio (Eu/Tb)		Molecular formula
	Theoretical	Measured	
1a	1/9	3.15/24.71	$Eu_{0.23}Tb_{1.77}C_{28}N_2O_{14}H_{18}$
1b	3/7	7.25/18.86	$Eu_{0.56}Tb_{1.44}C_{28}N_2O_{14}H_{18}$
1c	5/5	13.30/14.35	$Eu_{0.96}Tb_{1.04}C_{28}N_2O_{14}H_{18}$
1d	7/3	19.35/9.60	$Eu_{1.34}Tb_{0.66}C_{28}N_2O_{14}H_{18}$
1e	9/1	23.43/3.21	$Eu_{1.76}Tb_{0.24}C_{28}N_2O_{14}H_{18}$

Table S2 Lanthanide geometry analysis using the Shape software.[a]

Ln^{3+}	D_{4d} SAP	C_{2v} TP	D_{2d} DD
1 Eu^{3+}	1.448	2.405	2.426
2 Tb^{3+}	1.386	2.362	2.369

The Shape software allows us to numerically evaluate the deviation of a particular structure from an ideal shape.[a] The numerical parameters on **Table S2** suggested how much the coordination geometry of Ln^{3+} deviates from the ideal eight-coordinated geometries, such as SAP, TP, and DD, respectively. The smaller of this deviation parameter means the closer the structure geometry to the ideal one. In our case, the smallest shape values with SAP suggest D_{4d} site symmetry.

[a] Zabrodsky, H.; Peleg, S.; Avnir, D. *J. Am. Chem. Soc.* **1992**, 114, 7843.
Avnir, D.; Katzenelson, O.; Keinan, S.; Pinsky, M.; Pinto, Y.; Salomon, Y.; Zabrodsky Hel-Or, H. In *Concepts in Chemistry: A Contemporary Challenge*; Rouvray, D. H., Ed.; Research Studies Press Ltd.: Taunton, England, **1996**.

Table S3 Selected bond lengths (Å) and angles (°).

1					
O4-Eu	2.286(2)	O4-Eu -O6	157.26(7)	$O5^3$-Eu -O7	143.24(7)
O7-Eu	2.420(2)	O4-Eu -$O1^6$	85.62(8)	$O5^3$-Eu -O6	122.20(7)
O6-Eu	2.542(2)	O4-Eu -$O5^3$	80.54(7)	$O5^3$-Eu -O5	74.94(8)
$O1^6$-Eu	2.372(2)	O4-Eu -O5	148.91(7)	$O2^7$-Eu -O7	143.84(7)
O5-Eu	2.589(2)	O4-Eu -$O2^7$	116.44(8)	$O2^7$-Eu -O6	74.70(7)
$O5^3$-Eu	2.402(2)	O4-Eu -$O3^5$	84.08(7)	$O2^7$-Eu -$O1^6$	137.30(7)
$O2^7$-Eu	2.364(2)	O4-Eu -O7	83.56(8)	$O2^7$-Eu -O5	73.93(7)
$O3^5$-Eu	2.329(2)	O7-Eu-O6	77.42(7)	$O2^7$-Eu -$O5^3$	72.46(7)
Eu···Eu^3	3.9631(4)	O7-Eu-O5	105.05(7)	$O3^5$-Eu -O7	72.78(8)
		O6-Eu-O5	50.74(6)	$O3^5$-Eu -O6	78.50(7)
		$O1^6$-Eu -O7	69.59(8)	$O3^5$-Eu -$O1^6$	141.83(8)
		$O1^6$-Eu -O6	99.11(7)	$O3^5$-Eu -$O5^3$	137.26(8)
		$O1^6$-Eu -O5	70.33(7)	$O3^5$-Eu -O5	126.98(7)
		$O1^6$-Eu -$O5^3$	76.30(8)	$O3^5$-Eu -$O2^7$	79.43(7)

[1]-X,+Y,1/2-Z; [2]-1/2-X,-1/2+Y,-1/2-Z; [3]-X,2-Y,-Z; [4]-1/2+X,3/2-Y,-1/2+Z; [5]-X,1-Y,-Z; [6]-1/2-X,1/2+Y,-1/2-Z; [7]1/2+X,3/2-Y,1/2+Z

2					
O1-Tb1	2.575(2)	$O1^{2}$-Tb1-O1	74.95(9)	$O5^{3}$-Tb1-$O1^{2}$	80.39(9)
$O1^{2}$-Tb1	2.382(2)	$O1^{2}$-Tb1-O2	122.81(8)	$O5^{3}$-Tb1-O1	148.87(8)
O2-Tb1	2.516(3)	$O1^{2}$-Tb1-O3	143.00(9)	$O5^{3}$-Tb1-O2	156.79(9)
O3-Tb1	2.394(3)	O2-Tb1-O1	51.19(8)	$O5^{3}$-Tb1-O3	83.50(9)
O4-Tb1	2.307(2)	O3-Tb1-O1	105.17(8)	$O5^{3}$-Tb1-O4	83.80(9)
$O5^{3}$-Tb1	2.265(3)	O3-Tb1-O2	77.04(9)	$O5^{3}$-Tb1-$O6^{6}$	85.54(9)
$O6^{6}$-Tb1	2.351(2)	O4-Tb1-$O1^{2}$	137.03(9)	$O5^{3}$-Tb1-$O7^{7}$	116.54(9)
$O7^{7}$-Tb1	2.330(2)	O4-Tb1-O1	127.30(8)	$O6^{6}$-Tb1-O1	70.37(8)
Tb1···$Tb1^{2}$	3.9363(4)	O4-Tb1-O2	78.56(8)	$O6^{6}$-Tb1-$O1^{2}$	75.98(9)
		O4-Tb1-O3	73.02(9)	$O6^{6}$-Tb1-O2	99.22(9)
		O4-Tb1-$O6^{6}$	142.12(9)	$O6^{6}$-Tb1-O3	69.71(9)
		O4-Tb1-$O7^{7}$	79.06(9)	$O7^{7}$-Tb1-$O1^{2}$	73.00(9)
		$O7^{7}$-Tb1-O3	143.57(9)	$O7^{7}$-Tb1-O1	73.95(8)
		$O7^{7}$-Tb1-$O6^{6}$	137.46(8)	$O7^{7}$-Tb1-O2	74.84(9)
^{1}-X,+Y,1/2-Z; ^{2}-X,1-Y,-Z; ^{3}-X,-Y,-Z; ^{4}1/2+X,1/2-Y,1/2+Z; ^{5}1/2-X,-1/2+Y,1/2-Z; ^{6}-1/2+X,1/2-Y,-1/2+Z; ^{7}1/2-X,1/2+Y,1/2-Z					